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(54) Title: **SUBSTRATE COATING FOR IMPROVED TONER TRANSFER AND ADHESION**

(57) Abstract: A printing method comprising: providing a substrate having a surface coated with a coating comprising at least 25% silica; and printing on the coated surface with an ink comprising pigmented polymer particles and a carrier liquid.

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SUBSTRATE COATING FOR IMPROVED TONER TRANSFER AND ADHESION**FIELD OF THE INVENTION**

This invention is concerned with primers used for printing and more particularly with primers that have high affinity for both the ink and plastic such as used in substrates and compact disks (CD's).

BACKGROUND OF THE INVENTION

Primers or binders are generally necessary when printing with liquid toners on some plastic materials, such as PET, polycarbonate or other substrates. Without binders, such toners do not adhere well to the surface to be printed upon. Thus, a binder material is needed that has a high affinity for both the toner and the plastic. In the past, solvent based primers were used. However, the solvents in use are not environmentally friendly and are therefore commercially problematic.

However, it is difficult to provide a primer that is environmentally friendly and nonetheless has a high affinity for both the toner and the plastic. In general, it has been found that binders which are applied dissolved in solvents, which evaporate and leave a cured binder work best for this task. Such binders are generally acrylates. However, such primer systems do cause air pollution when the solvents evaporate.

Primers which are UV cured and/or applied in an aqueous solution are advantageous since they are non-polluting. Acrylic based monomers are known for use as UV cured binders. It is known to use hyrolized PVA (applied as a aqueous solution) for a binder. However, such binders, while they adhere well to plastic substrates, do not adhere well to toners such as those based on Nucrel (copolymers of ethylene and an alpha, beta ethelenically susaturated acid of either acrylic or metacrylic acid by E. I. du Pont) and Surlyn (ionomer resins by E. I. du Pont) polymers . Such polymer based toners are sold, for example, by Indigo, N.V. of the Netherlands under the trade name ElectroInk. The ElectroInk brand toners comprise pigmented polymer particles, a carrier liquid such as a Isopar (solvent of branched-chain aliphatic hydrocarbons and mixtures thereof, e.g., isoparapffinic hydrocarbon fractions by EXXON) or Marcol (highly refined petroleum oils by EXXON).

SUMMARY OF THE INVENTION

An aspect of the invention is concerned with the modification of presently available binders which are not solvent based to improve the adhesion of toner materials to them.

In some preferred embodiments of the invention, these available binders are acrylic based monomers. In some preferred embodiments of the invention, the available binders are UV cured. In some preferred embodiments of the invention, the binders are not dissolved in

organic solvents when they are applied. In some preferred embodiments of the invention, the binders have more than one of these characteristics.

An aspect of some preferred embodiments of the invention is concerned with the provision of a UV cured binder which has high adhesion to plastic substrates and also to toner materials, such as the aforementioned ElectroInk brand materials.

In a preferred embodiment of the invention, the binder comprises a high concentration of a material which absorbs the carrier liquid. In preferred embodiments of the invention, nano-silica (5-50 nanometers) is used as the absorber. Such particles should be preferably present in a concentration of at least 25 percent, more preferably between 30 and 50 percent and most preferably 35 and 45 percent. These percentages are by weight of total solids after curing.

While the exact operation of this absorber material is not known, it is believed that the addition of this material to the binder and the subsequent drawing of the toner to the binder by the material enables close approach of the toner polymer to the binder, such that strong, but very short range, Van der Waals forces take effect. Such forces strongly bind the toner polymer to the binder. Without the addition of the material, repulsion caused by the acid nature of both toner particles and binder is believed to mitigate the effect of such forces. However, the exact nature of the mechanism that obviates the use of said binders in the prior art is not yet established.

In a preferred embodiment of the invention, anchorage agents such as an amine material, especially diamine terminated polyoxyethelene, diamene, triamine or monoamine terminated Polypropylene oxide, are added to the binder coatings to increase their adhesion to the toner materials. Other anchorage agents can also be used, especially those with an amino terminated polymer backbone.

In a preferred embodiment of the invention, the binders comprise acrylic based UV curable monomers with mono, di and tri functionality. As indicated above, such binders, by themselves, are generally ineffective for use with negatively charged toners.

An aspect of some preferred embodiment of the invention is concerned with the addition of carrier liquid absorbing materials such as nano-silica, to other, non-UV cured binder materials such as, for example, water soluble hydrolized PVA. It was found that at high proportions of nano-silica, such as for example 25 percent or more by weight of total solids, the coating started to become "tonerphilic", in terms of transfer and adhesion to the binder.

There is thus provided, in accordance with a preferred embodiment of the invention, a printing method comprising:

providing a substrate having a surface coated with a coating comprising at least 25% silica; and

printing on the coated surface with an ink comprising pigmented polymer particles and a carrier liquid.

5 Preferably the coating comprises an acrylic material, for example a cross-linked polyacrylic ester.

Preferably, the coating is UV cured.

In various preferred embodiments of the invention the silica content of the coating comprises at least 30% silica, at least 35% silica, at least 40% silica, at least 45% silica and at
10 least 50% silica.

In various preferred embodiments of the invention the silica has a size of between 5 and 50 nanometers, between 10 and 40 nanometers, between 10 and 20 nanometers or about 16 nanometers.

In a preferred embodiment of the invention, the silica is not chemically bonded to the
15 rest of the coating. Alternatively, the silica is chemically bonded to the rest of the coating.

Preferably the coating further comprises an anchorage agent. Preferably, the anchorage agent comprises an amine material. Preferred amine materials include diamine, monoamine and triamine terminated substances. Preferably the substance is Poly(propylene oxide) or Polyoxylthelene.

20 In a preferred embodiment of the invention, the substrate and the pigmented particles are both acidic.

In a preferred embodiment of the invention the substrate is coated with a polyamide coating between the coating containing silica and the substrate.

In various preferred embodiments of the invention, the substrate is PVC, PET or
25 Polycarbonate.

Preferably, the coating forms a substantially smooth surface.

In a preferred embodiment of the invention, the substrate is a sheet of material. In an alternative preferred embodiment it is a disk, such as a CD disk.

There is further provided a substrate comprising:

30 a sheet of polymer; and

a substantially smooth printable coating on the polymer sheet comprising at least 25% silica.

Preferably the coating comprises an acrylic material, for example a cross-linked polyacrylic ester.

Preferably, the coating is UV cured.

In various preferred embodiments of the invention the silica content of the coating comprises at least 30% silica, at least 35% silica, at least 40% silica, at least 45% silica and at least 50% silica.

5 In various preferred embodiments of the invention the silica has a size of between 5 and 50 nanometers, between 10 and 40 nanometers, between 10 and 20 nanometers or about 16 nanometers.

In a preferred embodiment of the invention, the silica is not chemically bonded to the rest of the coating. Alternatively, the silica is chemically bonded to the rest of the coating.

10 Preferably the coating further comprises an anchorage agent. Preferably, the anchorage agent comprises an amine material. Preferred amine materials include diamine, monoamine and triamine terminated substances. Preferably the substance is Poly(propylene oxide) or Polyoxylthelene.

In a preferred embodiment of the invention, the substrate is acidic.

15 In a preferred embodiment of the invention the substrate is coated with a polyamide coating between the coating containing silica and the substrate.

In various preferred embodiments of the invention, the substrate is PVC, PET or Polycarbonate.

Preferably, the coating forms a substantially smooth surface.

20 There is further provided, in accordance with a preferred embodiment of the invention, a composition of matter comprising an acrylic monomer material comprising between 40% and 75% of the composition; and silica, in an amount exceeding 25% of the composition, which silica is not chemically bound to the monomer.

Preferably, the acrylic material comprises an acrylic ester.

25 Preferably, the monomer is UV curable.

In various preferred embodiments of the invention the silica content of the composition comprises at least 30% silica, at least 35% silica, at least 40% silica, at least 45% silica and at least 50% silica.

30 In various preferred embodiments of the invention the silica has a size of between 5 and 50 nanometers, between 10 and 40 nanometers, between 10 and 20 nanometers or about 16 nanometers.

In a preferred embodiment of the invention, the silica is not chemically bonded to the rest of the composition. Alternatively, the silica is chemically bonded to the rest of the composition.

Preferably the composition further comprises an anchorage agent. Preferably, the anchorage agent comprises an amine material. Preferred amine materials include diamine, monoamine and triamine terminated substances. Preferably the substance is Poly(propylene oxide) or Poly-oxyelthelene.

5 The invention will be more clearly understood with reference to the following non-limiting examples of preferred embodiments thereof.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The present invention is believed to be applicable to a wide range of binder materials, substrates and toner materials. Some representative, non-limiting, examples of the application
10 of the present invention follow.

Example 1

Various amounts of nano-silica (Aerosil R972 by Degussa) was dispersed in UV curable acrylic esters (Cray Valley Pro 2698). Aerosil R972 is a nanometric hydrophobic silica material having a particle size of approximately 16 nanometers. Other sizes, such as between 5
15 and 50 nanometers are also believed to be useful in the practice of the invention. Since the addition of silica to the acrylic monomer increases its viscosity, isopropyl alcohol (IPA) was added to the dispersion so that it could be coated onto a substrate. A wide range of acrylic esters are useful in the practice of the invention.

The dispersions were wire rod coated on 330 micrometer thick PVC sheets pre-coated
20 with PA polyamide (Mazzuccelli) and exposed to light from a UV mercury lamp which provides 118 watts/cm and passes the light source at a velocity of about 8.64 cm/sec or about 13.6 joules/cm². (A lamp having a power of 300 w/inch and motion of the substrate at a rate of 17 ft/min.) The resulting coated material was used as a substrate, for ElectroInkTM type 3.1 ink (liquid toner comprising pigmented toner particles and carrier liquid) of IndigoTM, N.V.,
25 on an OmniusTM CardPressTM printer of the same company. In this printer a liquid toner image is developed on a photoreceptor and transferred to an intermediate transfer member for subsequent transfer to the substrate by heat and pressure. During the second transfer process the image is also fused and fixed to the substrate.

The tested formulations (all parts are by weight) and the results are:

	Parts Acrylic Ester	Parts Silica	Parts IPA	NVS	Results
Control 1	10	0	1	91%	No transfer to substrate
Control 2	8	0	3	73%	No transfer to substrate
A	10.4	1 (9%)	1	92%	No transfer to substrate
B	5	1 (16.7%)	1.75	77.5%	Traces of ink transferred
C	2.5	1 (29%)	2	64%	Good transfer and fixing
D	1.5	1 (40%)	1.75	60%	Good transfer and fixing

In the table, NVS is the percentage of non-volatile solids in the coating mixture and the percentages under silica are percent silica of the NVS. All proportions in these and other examples are by weight. For dispersion D, the coating was somewhat uneven due to the large amount of silica in the coating. However, the transfer and fixing were good. The fixing was poor immediately after transfer but improved to good within a week after printing. From the table it appears that the coating changes from "tonerophobic" to "tonerophilic" at about 25% silica loading and that when transfer is good so is fixing.

Example 2

Various amounts of nano-silica (Aerosil R972 by Degussa) was dispersed in an aqueous acrylic copolymer solution (Glascol LS16, Allied Colloids-about 30% NVS). Aerosil R972 is a nanometric hydrophobic silica material having a particle size of approximately 16 nanometers. Other sizes, such as between 5 and 50 nanometers are also believed to be useful in the practice of the invention. The dispersions were homogenized in a high shear mixer for 1-3 minutes. The dispersions were diluted with water for high proportions of silica, their viscosity made them difficult to homogenize.

The dispersions were wire rod coated onto PET films and dried at elevated temperature (about 60°C to form a film. The resulting coated material was used as a substrate, for ElectroInk™ type 3.1 ink (liquid toner comprising pigmented toner particles and carrier liquid) of Indigo™, N.V., on an Omnius™ CardPress™ printer of the same company.

The following table summarizes the results:

	Total weight	Wt. acrylic	Wt. Silica	NVS	Results
A	180.3	52.5	5.3 (9%)	32%	Only traces of transfer
B	176.7	42	8.7 (17%)	29%	Only traces of transfer
C	158.2	36.8	11.2 (23%)	32%	Only traces of transfer
D	145	29	14.5 (33%)	31%	Good Transfer, Poor Fixing
E	170	22	15 (40%)	22%	Good Transfer, Good Fixing

Coatings D and E resulted in a hazy, rather than clear coating. This may be acceptable for some applications. However, the haziness may be removed by overcoating the film with clear varnish, for example a UV cured varnish. This coating process results in the filling in of the unevenness of the surface caused by the silica, which results in the haziness of the coating.

- 5 From the table it appears that the coating changes from tonerophobic to tonerophilic at about 25-30% silica loading and that when fixing is good for loading of 35-40% or greater.

Example 3

Various amounts of nano-silica (Aerosil R972 by Degussa) was dispersed in an aqueous styrene-acrylic emulsion (Zinpol 280, Worlee-about 48% NVS). Aerosil R972 is a nanometric hydrophobic silica material having a particle size of approximately 16 nanometers. Other sizes, such as between 5 and 50 nanometers are also believed to be useful in the practice of the invention. The dispersions were homogenized in a high shear mixer for 1-3 minutes. The dispersions were diluted with water when for high proportions of silica, when their viscosity made them difficult to homogenize.

- 15 The resulting coated material was used as a substrate, for ElectroInk™ type 3.1 ink (liquid toner comprising pigmented toner particles and carrier liquid) of Indigo™, N.V., on an Omnius™ CardPress™ printer of the same company.

The following table summarizes the results:

	Total weight	Wt. acrylic	Wt. Silica	NVS	Results
A	186.5	43.2	6.5 (13%)	27%	Suffer from Foaming
B	153.7	35	8.7 (20%)	28%	Suffer from Foaming
C	164	27.1	9 (25%)	22%	Only traces of transfer
D	140.3	22.6	11.3 (33%)	24%	Good Transfer, Fair Fixing
E	158.4	18.9	13.4 (42%)	20%	Good Transfer, Good Fixing

- 20 A and B suffered from foaming causing an uneven coating. C produced a transparent film, but transfer to it was poor. Coatings D and E resulted in a hazy, rather than clear coating. This may be acceptable for some applications. However, the haziness may be removed by overcoating the film with clear varnish. This coating process results in the filling in of the unevenness of the surface caused by the silica, which results in the haziness of the coating. From the table it appears that the coating changes from tonerophobic to tonerophilic at about 30% silica loading and that fixing is good starting at about 40% loading.
- 25

Example 4

Various amounts of nano-silica (Aerosil R972 by Degussa) was dispersed in an aqueous PVA solution formed by dissolving polyvinyl alcohol (Aldrich 88% hydrolized- average molecular weight 85k-146k) in deionized water to give a 10% solution. Aerosil R972 is a nanometric hydrophobic silica material having a particle size of approximately 16 nanometers. Other sizes, such as between 5 and 50 nanometers are also believed to be useful in the practice of the invention. The dispersions were homogenized in a high shear mixer for 1-3 minutes. Water was added to reduce the viscosity when it was too high for coating.

The resulting coated material was used as a substrate, for ElectroInk™ type 3.1 ink (liquid toner comprising pigmented toner particles and carrier liquid) of Indigo™, N.V., on an Omnius™ CardPress™ printer of the same company.

The following table summarizes the results:

	Total weight	Wt. PVA	Wt. Silica	NVS	Results
A	204.5	15	4.5 (23%)	10%	Poor transfer, Very Poor Fixing
B	139	10	5 (33%)	11%	Fair Transfer, Poor Fixing
C	140	10	6 (37.5%)	11%	Fair Transfer, Poor Fixing
D	307	10	7 (41%)	6%	Good Transfer, Poor Fixing
E	209	10	9 (47.3%)	9%	Good Transfer, Good Fixing

From the table it appears that the coating changes from tonerophobic to tonerophilic at about 30% silica loading and that fixing is good only for loadings above about 45%.

Example 5

Highlink OG materials (Clariant) are liquid suspensions of grafted colloidal silica in 1,6-hexanediol diacrylate. Among other organasols which are available are OG 100 in which the organic modifier is 2-Hydroxyethyl methacrylate, OG 101 in which the organic modifier is 2-Hydroxyethyl acetate, OG 103 in which the organic modifier is 1,6-Hexanediol diacrylate and OG 108 in which the modifier is Tripropylene glycol diacrylate. Each of these materials is available in various proportions of modifier and silica, ranging from 30 to 50 percent silica by weight. Since the silica is grafted, the viscosity is lower than for mixtures of ungrafted silica.

To 89 grams of Highlink OG 103-53 (51±1% by weight silica) was added 10 grams of Irgacure 651 organic photo-initiator (Ciba) and the materials were mixed until the initiator was totally dissolved in the carrier of the Highlink material. To this mixture 10 grams of Poly(propylene oxide), diamine terminated (molecular weight 230-Scientific Polymer Products) was added to form a coating material.

This coating material was used to polycarbonate disks (CDI, Ltd.) and Melinex 529 PET films (ICI) by screen printing using a 180 mesh/cm fabric screen. The coating was cured immediately by applying to it light from a 118 watts/cm UV/lamp source and passing the coating by the light source at a velocity of about 5.08 cm/sec or about 23.2 joules/cm² (A lamp having a power of 300 w/inch and motion of the substrate at a rate of 10 ft/min.) The coating weight was about 5.3 gm/m².

These coated materials were printed on the OmniusTM CardPressTM printer using ElectroInk type 3.1 ink. Transfer and fixing were excellent. Variations of the amounts of additives (diamine 5-20% by weight of the Highlink material and initiator 2-15% by weight of the Highlink material gave good results.

When the Highlink OG 108-53 was replaced by Highlink OG 108-31 (30% silica by weight), the toner did not transfer well to the coated material.

Various amine anchorage agents were used in various experiments to determine their suitability. To 45 gr. Highlink OG 103-53 were added 2.5 grams of Irgacure 184 (CIBA) photoinitiator. The mixture was mixed until the powder was totally incorporated. Then in various experiments 2.5 grams of diamine terminated Poly(propylene oxide) (molecular weight 230, amine content 8.45 meq.), monoamine terminated Poly(propylene oxide) (molecular weight 600, amine content 1.66 meq.) or triamine terminated Poly(propylene oxide) (molecular weight 480, amine content 6.45 meq.). The various materials were wire rod coated onto Melinex PET films. The coating was cured immediately by exposure to about 46 joules/cm² of UV light. The coating weight was estimated at about 15 gm/m².

These coated PET sheets were printed on in an OmniusTM CardPressTM printer. All the samples showed good transfer of toner to the sheets. The diamine showed good fixing, the triamine showed good to fair fixing and the monoamine showed only fair fixing.

These results demonstrate the dependence of adhesion fixing characteristics on the amine content of the coating.

The present invention has been described with reference to the best mode for carrying out the invention known to the inventors at the time of filing and using toner and printing systems which are readily available to them. It should be understood that the present invention is believed to be applicable to a wide variety of toners, binders and substrate. As used herein, the terms "include" "have" and "comprise" and their conjugates mean "including but not necessarily limited to".

CLAIMS

1. A printing method comprising:
providing a substrate having a surface coated with a coating comprising at least 25%
5 silica; and
printing on the coated surface with an ink comprising pigmented polymer particles and
a carrier liquid.
2. A printing method according to claim 1 wherein the coating comprises an acrylic
10 material.
3. A printing method according to claim 2 wherein the acrylic material comprises a cross-
linked polyacrylic ester.
- 15 4. A printing method according any of the preceding claims wherein the coating is UV
cured.
5. A printing method according to any of the preceding claims wherein the coating
comprises at least 30% silica.
20
6. A printing method according to claim 5 wherein the coating comprises at least 35%
silica.
7. A printing method according to claim 6 wherein the coating comprises at least 40%
25 silica.
8. A printing method according to claim 7 wherein the coating comprises at least 45%
silica.
- 30 9. A printing method according to claim 8 wherein the coating comprises at least 50%
silica.
10. A printing method according to any of the preceding claims wherein the silica has a
size of between 5 and 50 nanometers.

11. A printing method according to claim 10 wherein the silica has a size of between 10 and 40 nanometers.

5 12. A printing method according to claim 11 wherein the silica has a size of between 10 and 20 nanometers.

13. A printing method according to claim 12 wherein the silica has a size of about 16 nanometers.

10 14. A printing method according to any of the preceding claims wherein the silica is not chemically bonded to the rest of the coating.

15 15. A printing method according to any of claims 1-13 wherein the silica is chemically bonded to the rest of the coating.

16. A printing method according to any of the preceding claims wherein the coating further comprises an anchorage agent.

20 17. A printing method according to claim 16 wherein the anchorage agent comprises an amine material.

18. A printing method according to claim 17 wherein the amine material comprises a diamine terminated substance.

25 19. A printing method according to claim 17 wherein the amine material comprises a monoamine terminated substance.

30 20. A printing method according to claim 17 wherein the amine material comprises a triamine terminated substance.

21. A printing method according to any of claims 18-20 wherein the substance is Poly(propylene oxide).

22. A printing method according to claim 18 wherein the substance is Poly-oxyelthelene.

23. A printing method according to any of the preceding claims wherein the substrate and
5 the pigmented particles are both acidic.

24. A printing method according to any of the preceding claims wherein the substrate is coated with a polyamide coating between the coating containing silica and the substrate.

10 25. A printing method according to any of the preceding claims wherein the substrate is PVC.

26. A printing method according to any of claims 1-24 wherein the substrate is PET.

15 27. A printing method according to any of claims 1-24 wherein the substrate is polycarbonate.

28. A printing method according to any of the preceding claims wherein the coating forms a substantially smooth surface.

20 29. A printing method according to any of the preceding claims wherein the substrate is a sheet of material.

30. A printing method according to any of claims 1-28 wherein the substrate is a disk.

25 31. A substrate comprising:
a sheet of polymer; and
a substantially smooth printable coating on the polymer sheet comprising at least 25% silica.

30 32. A coated substrate according to claim 31 wherein the coating comprises an acrylic material.

33. A coated substrate according to claim 32 wherein the acrylic material comprises a cross-linked polyacrylic ester.

34. A coated substrate according any of claims 31-33 wherein the coating is UV cured.

35. A coated substrate according to any of claims 31-34 wherein the coating comprises at least 30% silica.

36. A coated substrate according to claim 35 wherein the coating comprises at least 35% silica.

37. A coated substrate according to claim 36 wherein the coating comprises at least 40% silica.

38. A coated substrate according to claim 37 wherein the coating comprises at least 45% silica.

39. A coated substrate according to claim 38 wherein the coating comprises at least 50% silica.

40. A coated substrate according to any of claims 31-39 wherein the silica has a size of between 5 and 50 nanometers.

41. A coated substrate according to claim 40 wherein the silica has a size of between 10 and 40 nanometers.

42. A coated substrate according to claim 41 wherein the silica has a size of between 10 and 20 nanometers.

43. A coated substrate according to claim 42 wherein the silica has a size of about 16 nanometers.

44. A coated substrate according to any of claims 31-43 wherein the silica is not chemically bound to the rest of the coating.

45. A coated substrate according to any of claims 31-43 wherein the silica is chemically bound to the rest of the coating.

5 46. A coated substrate according to any of claims 31-44 wherein the coating further comprises an anchorage agent.

47. A coated substrate according to claim 46 wherein the anchorage agent comprises an amine material.

10 48. A coated substrate according to claim 47 wherein the amine material comprises a diamine terminated substance.

15 49. A coated substrate according to claim 47 wherein the amine material comprises a monoamine terminated substance.

50. A coated substrate according to claim 47 wherein the amine material comprises a triamine terminated substance.

20 51. A coated substrate according to any of claims 48-50 wherein the substance is Poly(propylene oxide).

52. A printing method according to claim 48 wherein the substance is Poly-oxylthelene.

25 53. A coated substrate according to any of claims 31-52 wherein the substrate is acidic.

54. A coated substrate according to any of claims 31-52 wherein the substrate is coated with a polyamide coating between the coating containing silica and the sheet.

30 55. A coated substrate according to any of claims 31-54 wherein the sheet is PVC.

56. A coated substrate according to any of claims 31-54 wherein the sheet is PET.

57. A coated substrate according to any of claims 31-54 wherein the sheet is polycarbonate.
58. A composition of matter comprising an acrylic monomer material comprising between 40% and 75% of the composition; and silica, in an amount exceeding 25% of the composition, which silica is not chemically bound to the monomer.
59. A composition according to claim 58 wherein the acrylic material comprises an acrylic ester.
60. A composition according to any claim 58 or claim 59 wherein the monomer is UV curable.
61. A composition according to any of claims 58-60 comprising at least 30% silica.
62. A composition according to any of claims 58-60 comprising at least 35% silica.
63. A composition according to any of claims 58-60 comprising at least 40% silica.
64. A composition according to any of claims 58-60 comprising at least 45% silica.
65. A composition according to any of claims 58-60 comprising at least 50% silica.
66. A composition according to any of claims 58-65 wherein the silica has a size of between 5 and 50 nanometers.
67. A composition according to any of claims 58-66 wherein the silica has a size of between 10 and 40 nanometers.
68. A composition according to any of claims 58-66 wherein the silica has a size of between 10 and 20 nanometers.
69. A composition according to any of claims 58-68 wherein the silica has a size of about 16 nanometers.

70. A composition according to any of claims 58-69 wherein the silica is not chemically bound to the rest of the composition.

5 71. A composition according to any of claims 58-69 wherein the silica is chemically bound to the rest of the composition.

72. A composition according to any of claims 58-71 wherein the composition further comprises an anchorage agent.

10

73. A composition according to claim 72 wherein the anchorage agent comprises an amine material.

15

74. A composition according to claim 73 wherein the amine material comprises a diamine terminated substance.

75. A composition according to claim 73 wherein the amine material comprises a monoamine terminated substance.

20

76. A composition according to claim 73 wherein the amine material comprises a triamine terminated substance.

77. A composition according to any of claims 73-76 wherein the substance is Poly(propylene oxide).

25

78. A printing method according to claim 74 wherein the substance is Poly-oxyelthelene.

INTERNATIONAL SEARCH REPORT

In **ational Application No**

PCT/IL 99/00510

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 G03G7/00 G03G9/12 G03G9/13 B41M5/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 G03G B41M G03F C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 789 281 A (MOBIL OIL CORP) 13 August 1997 (1997-08-13) page 2, line 53 -page 3, line 20 page 3, line 45 - line 50 page 6, line 34	1,2,5-9, 14,28, 29,31, 32, 35-39,44
X	EP 0 892 008 A (UCB SA) 20 January 1999 (1999-01-20) page 2, line 54 -page 4, line 4 -/-	31-33, 35-39, 44,53, 58,59, 61-65,70

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

16 May 2000

Date of mailing of the international search report

24/05/2000

Name and mailing address of the ISA

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Authorized officer

Vogt, C

INTERNATIONAL SEARCH REPORT

International Application No

PCT/IL 99/00510

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 012, no. 243 (P-728), 9 July 1988 (1988-07-09) & JP 63 033749 A (DYNIC CORP), 13 February 1988 (1988-02-13) abstract	31, 32, 35-39, 44
X	EP 0 507 998 A (MOORE BUSINESS FORMS INC) 14 October 1992 (1992-10-14) claims 1, 15	31, 35-39, 44
X	DATABASE WPI Section Ch, Week 199728 Derwent Publications Ltd., London, GB; Class A89, AN 1997-302654 XP002137702 & JP 09 114122 A (DYNIC CORP), 2 May 1997 (1997-05-02) abstract	1, 2, 5-9, 14, 28, 29, 31, 32, 35-39, 44
X	US 5 612 281 A (KOBAYASHI TAKASHI ET AL) 18 March 1997 (1997-03-18) column 11 -column 12; example 1	31, 35-40, 44
X	DATABASE WPI Section Ch, Week 199734 Derwent Publications Ltd., London, GB; Class A14, AN 1997-369487 XP002137736 & JP 09 157315 A (DAICEL-UCB KK), 17 June 1997 (1997-06-17) abstract	58, 60-65, 70

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/IL 99/00510

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0789281	A	13-08-1997	US 5827627 A US 5789123 A AU 706673 B AU 7427596 A BR 9700938 A CA 2194524 A JP 9329909 A	27-10-1998 04-08-1998 24-06-1999 21-08-1997 01-09-1998 13-08-1997 22-12-1997
EP 0892008	A	20-01-1999	AU 8326898 A WO 9903916 A	10-02-1999 28-01-1999
JP 63033749	A	13-02-1988	JP 2045474 C JP 7069627 B	09-04-1996 31-07-1995
EP 0507998	A	14-10-1992	AU 644512 B AU 1117692 A BR 9200668 A CA 2059077 A DE 69114122 D DE 69114122 T JP 2713832 B JP 5132898 A MX 9201293 A NZ 241126 A US 5437925 A US 5605725 A US 5622781 A US 5656369 A	09-12-1993 15-10-1992 24-11-1992 13-10-1992 30-11-1995 18-04-1996 16-02-1998 28-05-1993 01-10-1992 27-04-1994 01-08-1995 25-02-1997 22-04-1997 12-08-1997
JP 9114122	A	02-05-1997	NONE	
US 5612281	A	18-03-1997	JP 7276789 A	24-10-1995
JP 9157315	A	17-06-1997	NONE	

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From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

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PCT

NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL PRELIMINARY
EXAMINATION REPORT
(PCT Rule 71.1)

Date of mailing
(day/month/year) 21.12.2001

Applicant's or agent's file reference
PDX

IMPORTANT NOTIFICATION

International application No.
PCT/IL99/00510

International filing date (day/month/year)
22/09/1999

Priority date (day/month/year)
22/09/1999

Applicant
INDIGO N.V. et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.


4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/

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PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference PDX	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/IL99/00510	International filing date (day/month/year) 22/09/1999	Priority date (day/month/year) 22/09/1999
International Patent Classification (IPC) or national classification and IPC G03G7/00		
Applicant INDIGO N.V. et al.		


1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 7 sheets, including this cover sheet.

☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 6 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand 03/09/2000	Date of completion of this report 21.12.2001
Name and mailing address of the international preliminary examining authority:  European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016	Authorized officer Vogt, C Telephone No. +31 70 340 3706



INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/IL99/00510

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, pages:

1-9 as originally filed

Claims, No.:

1-60 with telefax of 10/10/2001

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

5. ☒ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/IL99/00510

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

see separate sheet

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	2-32,34-59
	No:	Claims	1,33,60
Inventive step (IS)	Yes:	Claims	15-24,47-56
	No:	Claims	1-14,25-46,57-60
Industrial applicability (IA)	Yes:	Claims	1-60
	No:	Claims	

2. Citations and explanations **see separate sheet**

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/IL99/00510

Re Item I

section I.5:

The amendments filed with demand dated 10.10.2001 introduce subject-matter which extends beyond the content of the application as filed (Article 34 (2) (b) PCT):

Claim 31: "A printing method according to any of the preceding claims wherein the surface of the coating is film."

Claim 33: "A substrate comprising a sheet of polymer, a printable coating in the form of a film on the polymer sheet comprising at least 25 % nano-silica by weight of total solids".

The amended features "a surface of the coating is film" and "a printable coating is in the form of a film" is not supported - in general - by the original disclosure.

Thus, no basis for present claims 31 and 33 can be found in the originally filed application.

Re Item V

Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. The subject matter of claims 31 and 33 filed with letter of 10.10.2001 has been interpreted as follows:

Claim 31: "A printing method according to any of the preceding claims wherein the coating forms a smooth surface". (original claim 28)

Claim 33: "A substrate comprising a sheet of polymer; and a smooth printable coating on the polymer sheet comprising at least 25 % nano-silica by weight of total solids". (original claim 31)

2. Reference is made to the following documents:

D1: US-A-5612281

D2: EP-A-789 281

D3: EP-A-892 008

D4: EP-A-507 998

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/IL99/00510

2. The term "liquid toner" in claim 1 covers "ink-jet inks" which are used in ink jet recording printing methods.

D1 relates to printing methods, such as ink-jet recording (col. 2, l. 58-60) providing a substrate having a surface coated with a coating comprising silica particles with a particle size of 10 nm and resin in the weight ratio between silica and resin of 1.5:1 to 10:1 (col. 3, l. 8 to 17) in the form of a porous film (col. 5, l. 56) and printing on the coated surface with an ink-jet ink, i.e. a liquid toner.

Thus, the subject matter of claims 1, 33 and 60 lacks novelty.

3. D2, which is considered to represent the most relevant state of the art, describes a printing method comprising providing a substrate having a (polymeric sheet) surface coated with a coating comprising "up to 80 wt% of micron sized silica" (see page 3, line 50) and printing on the coated surface with Electroink type liquid toner (see page 6, line 34) which is identical to the liquid toner of present application.

The subject matter of present claims 1 and 33 differs from the printing method and the substrate of D2 in the particle size of the silica, i.e. nanometric silica.

The problem to be solved by the present invention may therefore be regarded as finding (a printing method providing) a substrate with silica particles allowing a smoother coating of said printable coated substrate and thus leading to an improved adhesion of the liquid toner material and the coated substrate and furthermore an improved adhesion between the substrate and the coating-binder.

The solution proposed in claims 1 and 33 of the present application cannot be considered as involving an inventive step (Article 33(3) PCT).

The replacement of micron-sized silica particles by nanometric silica particles - as already mentioned in D1 - in order to increase to provide a coated substrate with a smooth surface is merely one of several straightforward possibilities from which the skilled person would select, in accordance with circumstances, without the exercise of inventive skill, in order to solve the problem posed:

The specific lower weight limit of 25 % of silica particles in combination with the specific

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/IL99/00510

selection of the silica particle size can be seen as merely the result of optimisation of two parameters which led to a compromise lying within the skilled person's discretion. Such compromises in the case of a parameter optimisation were not deemed to be surprising and their discovery was thus not considered to involve an inventive step. Thus, the subject matter of independent claims 1 and 33 lacks an inventive step.

The additional features of dependent claims 2, 5 to 9, 14, 28, 29, 31, 32, 37 to 41, 46 and 60 are also disclosed in D2. Thus, the subject matter of claims 2, 5 to 9, 14, 28, 29, 31, 32, 37 to 41, 46 and 60 lacks an inventive step.

In dependent claims 3, 4, 10 to 13, 25 to 27, 30, 34 to 36, 42 to 45, 57 to 59 a slight constructional change in the printing method/ substrate of claims 1 and 33 is defined which comes within the scope of the customary practice followed by persons skilled in the art, especially as the advantages thus achieved can readily be foreseen. Consequently, the subject-matter of claims 3, 4, 10 to 13, 25 to 27, 30, 34 to 36, 42 to 45, 57 to 59 also lack an inventive step with regard to D2, since no sound evidence was provided that the features of said dependent claims involve a surprising effect, i.e. involve an inventive step.

Dependent claims 15 to 24 and 47 to 56 appear to contain features which, in combination with the features of any claim to which they refer, meet the requirements of the PCT in respect of novelty and/ or inventive step with regard to the available prior art.

5. For the same reasons the subject matter of claims 1 and 33 lacks an inventive step with regard to D3 (page 2, line 54 to page 4, line 4; page 3, l. 38 - 45) which a plastic film coated on a substrate comprising a coating composition which contains an acrylic (ester) monomer and silica in a content up to 85 wt. %.

6. For the same reasons the subject matter of claims 1, 2, 5 to 9, 14, 28, 33, 34, 37 to 41 and 46 lacks an inventive step with regard to D4, which describes a coated

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/IL99/00510

substrate comprising a polymeric sheet covered with a coating layer comprising acrylate resin and silica in a content up to 75 wt% and a coated substrate comprising a polymeric sheet covered with a coating layer comprising 50 to 95 parts by dry weight of silica and 5 to 50 parts by dry weight of binder.

CLAIMS

1. A printing method comprising:
providing a substrate having a surface coated with a coating comprising at least 25%
5 silica; and
printing on the coated surface with an ink comprising pigmented polymer particles and
a carrier liquid.
2. A printing method according to claim 1 wherein the coating comprises an acrylic
10 material.
3. A printing method according to claim 2 wherein the acrylic material comprises a cross-
linked polyacrylic ester.
- 15 4. A printing method according any of the preceding claims wherein the coating is UV
cured.
5. A printing method according to any of the preceding claims wherein the coating
comprises at least 30% silica.
20
6. A printing method according to claim 5 wherein the coating comprises at least 35%
silica.
7. A printing method according to claim 6 wherein the coating comprises at least 40%
25 silica.
8. A printing method according to claim 7 wherein the coating comprises at least 45%
silica.
- 30 9. A printing method according to claim 8 wherein the coating comprises at least 50%
silica.
10. A printing method according to any of the preceding claims wherein the silica has a
size of between 5 and 50 nanometers.

11. A printing method according to claim 10 wherein the silica has a size of between 10 and 40 nanometers.

5 12. A printing method according to claim 11 wherein the silica has a size of between 10 and 20 nanometers.

13. A printing method according to claim 12 wherein the silica has a size of about 16 nanometers.

10 14. A printing method according to any of the preceding claims wherein the silica is not chemically bonded to the rest of the coating.

15 15. A printing method according to any of claims 1-13 wherein the silica is chemically bonded to the rest of the coating.

16. A printing method according to any of the preceding claims wherein the coating further comprises an anchorage agent.

20 17. A printing method according to claim 16 wherein the anchorage agent comprises an amine material.

18. A printing method according to claim 17 wherein the amine material comprises a diamine terminated substance.

25 19. A printing method according to claim 17 wherein the amine material comprises a monoamine terminated substance.

30 20. A printing method according to claim 17 wherein the amine material comprises a triamine terminated substance.

21. A printing method according to any of claims 18-20 wherein the substance is Poly(propylene oxide).

22. A printing method according to claim 18 wherein the substance is Poly-oxyelthelene.

23. A printing method according to any of the preceding claims wherein the substrate and
5 the pigmented particles are both acidic.

24. A printing method according to any of the preceding claims wherein the substrate is coated with a polyamide coating between the coating containing silica and the substrate.

10 25. A printing method according to any of the preceding claims wherein the substrate is PVC.

26. A printing method according to any of claims 1-24 wherein the substrate is PET.

15 27. A printing method according to any of claims 1-24 wherein the substrate is polycarbonate.

28. A printing method according to any of the preceding claims wherein the coating forms a substantially smooth surface.

20 29. A printing method according to any of the preceding claims wherein the substrate is a sheet of material.

30. A printing method according to any of claims 1-28 wherein the substrate is a disk.

25 31. A substrate comprising:
a sheet of polymer; and
a substantially smooth printable coating on the polymer sheet comprising at least 25% silica.

30 32. A coated substrate according to claim 31 wherein the coating comprises an acrylic material.

33. A coated substrate according to claim 32 wherein the acrylic material comprises a cross-linked polyacrylic ester.

34. A coated substrate according any of claims 31-33 wherein the coating is UV cured.

35. A coated substrate according to any of claims 31-34 wherein the coating comprises at least 30% silica.

36. A coated substrate according to claim 35 wherein the coating comprises at least 35% silica.

37. A coated substrate according to claim 36 wherein the coating comprises at least 40% silica.

38. A coated substrate according to claim 37 wherein the coating comprises at least 45% silica.

39. A coated substrate according to claim 38 wherein the coating comprises at least 50% silica.

40. A coated substrate according to any of claims 31-39 wherein the silica has a size of between 5 and 50 nanometers.

41. A coated substrate according to claim 40 wherein the silica has a size of between 10 and 40 nanometers.

42. A coated substrate according to claim 41 wherein the silica has a size of between 10 and 20 nanometers.

43. A coated substrate according to claim 42 wherein the silica has a size of about 16 nanometers.

44. A coated substrate according to any of claims 31-43 wherein the silica is not chemically bound to the rest of the coating.

45. A coated substrate according to any of claims 31-43 wherein the silica is chemically bound to the rest of the coating.

5 46. A coated substrate according to any of claims 31-44 wherein the coating further comprises an anchorage agent.

47. A coated substrate according to claim 46 wherein the anchorage agent comprises an amine material.

10 48. A coated substrate according to claim 47 wherein the amine material comprises a diamine terminated substance.

49. A coated substrate according to claim 47 wherein the amine material comprises a
15 monoamine terminated substance.

50. A coated substrate according to claim 47 wherein the amine material comprises a triamine terminated substance.

20 51. A coated substrate according to any of claims 48-50 wherein the substance is Poly(propylene oxide).

52. A printing method according to claim 48 wherein the substance is Poly-oxyethylthelene.

25 53. A coated substrate according to any of claims 31-52 wherein the substrate is acidic.

54. A coated substrate according to any of claims 31-52 wherein the substrate is coated with a polyamide coating between the coating containing silica and the sheet.

30 55. A coated substrate according to any of claims 31-54 wherein the sheet is PVC.

56. A coated substrate according to any of claims 31-54 wherein the sheet is PET.

57. A coated substrate according to any of claims 31-54 wherein the sheet is polycarbonate.
58. A composition of matter comprising an acrylic monomer material comprising between 40% and 75% of the composition; and silica, in an amount exceeding 25% of the composition,
5 which silica is not chemically bound to the monomer.
59. A composition according to claim 58 wherein the acrylic material comprises an acrylic ester.
- 10 60. A composition according to any claim 58 or claim 59 wherein the monomer is UV curable.
61. A composition according to any of claims 58-60 comprising at least 30% silica.
- 15 62. A composition according to any of claims 58-60 comprising at least 35% silica.
63. A composition according to any of claims 58-60 comprising at least 40% silica.
64. A composition according to any of claims 58-60 comprising at least 45% silica.
20
65. A composition according to any of claims 58-60 comprising at least 50% silica.
66. A composition according to any of claims 58-65 wherein the silica has a size of between 5 and 50 nanometers.
25
67. A composition according to any of claims 58-66 wherein the silica has a size of between 10 and 40 nanometers.
68. A composition according to any of claims 58-66 wherein the silica has a size of
30 between 10 and 20 nanometers.
69. A composition according to any of claims 58-68 wherein the silica has a size of about 16 nanometers.

70. A composition according to any of claims 58-69 wherein the silica is not chemically bound to the rest of the composition.

5 71. A composition according to any of claims 58-69 wherein the silica is chemically bound to the rest of the composition.

72. A composition according to any of claims 58-71 wherein the composition further comprises an anchorage agent.

10

73. A composition according to claim 72 wherein the anchorage agent comprises an amine material.

15

74. A composition according to claim 73 wherein the amine material comprises a diamine terminated substance.

75. A composition according to claim 73 wherein the amine material comprises a monoamine terminated substance.

20 76. A composition according to claim 73 wherein the amine material comprises a triamine terminated substance.

77. A composition according to any of claims 73-76 wherein the substance is Poly(propylene oxide).

25

78. A printing method according to claim 74 wherein the substance is Poly-oxyelthelene.

10/088655
JC13 Rec'd PCT/PTO 14 MAR 2002CLAIMS

1. A printing method comprising:
providing a substrate having a surface coated with a coating comprising at least 25%
5 nano-silica by weight; and
printing on the coated surface with a liquid toner comprising pigmented polymer
particles and a carrier liquid.
2. A printing method according to claim 1 wherein the coating comprises an acrylic
10 material.
3. A printing method according to claim 2 wherein the acrylic material comprises a cross-
linked polyacrylic ester.
- 15 4. A printing method according any of the preceding claims wherein the coating is UV
cured.
5. A printing method according to any of the preceding claims wherein the coating
comprises at least 30% silica.
- 20 6. A printing method according to claim 5 wherein the coating comprises at least 35%
silica.
7. A printing method according to claim 6 wherein the coating comprises at least 40%
25 silica.
8. A printing method according to claim 7 wherein the coating comprises at least 45%
silica.
- 30 9. A printing method according to claim 8 wherein the coating comprises at least 50%
silica.
10. A printing method according to any of the preceding claims wherein the silica has a
size of between 5 and 50 nanometers.

11. A printing method according to claim 10 wherein the silica has a size of between 10 and 40 nanometers.
- 5 12. A printing method according to claim 11 wherein the silica has a size of between 10 and 20 nanometers.
13. A printing method according to claim 12 wherein the silica has a size of about 16 nanometers.
- 10 14. A printing method according to any of the preceding claims wherein the silica is not chemically bonded to the rest of the coating.
- 15 15. A printing method according to any of claims 1-13 wherein the silica is chemically bonded to the rest of the coating.
16. A printing method according to any of the preceding claims wherein the coating further comprises an anchorage agent.
- 20 17. A printing method according to claim 16 wherein the anchorage agent comprises an amine material.
18. A printing method according to claim 17 wherein the amine material comprises a diamine terminated substance.
- 25 19. A printing method according to claim 17 wherein the amine material comprises a monoamine terminated substance.
20. A printing method according to claim 17 wherein the amine material comprises a triamine terminated substance.
- 30 21. A printing method according to any of claims 18-20 wherein the substance is Poly(propylene oxide).

PDX A02

22. A printing method according to claim 18 wherein the substance is Poly-oxyethelene.
23. A printing method according to any of the preceding claims wherein the substrate and the pigmented particles are both acidic.
- 5 24. A printing method according to any of the preceding claims wherein the substrate is coated with a polyamide coating between the coating containing silica and the substrate.
- 10 25. A printing method according to any of the preceding claims wherein the substrate is PVC.
26. A printing method according to any of claims 1-24 wherein the substrate is PET.
- 15 27. A printing method according to any of claims 1-24 wherein the substrate is polycarbonate.
28. A printing method according to any of the preceding claims wherein the coating forms a substantially smooth surface.
- 20 29. A printing method according to any of the preceding claims wherein the substrate is a sheet of material.
30. A printing method according to any of claims 1-28 wherein the substrate is a disk.
- 25 31. A printing method according to any of the preceding claims wherein the surface of the coating is film.
32. A printing method according to claim 31 wherein the coating is smooth.
- 30 33. A substrate comprising:
a sheet of polymer; and
a printable coating in the form of a film, on the polymer sheet comprising at least 25% nano-silica by weight of total solids.

PDX A02

34. A coated substrate according to claim 33 wherein the coating comprises an acrylic material.
35. A coated substrate according to claim 34 wherein the acrylic material comprises a cross-linked polyacrylic ester.
36. A coated substrate according any of claims 33-35 wherein the coating is UV cured.
37. A coated substrate according to any of claims 33-36 wherein the coating comprises at least 30% silica.
38. A coated substrate according to claim 37 wherein the coating comprises at least 35% silica.
39. A coated substrate according to claim 38 wherein the coating comprises at least 40% silica.
40. A coated substrate according to claim 39 wherein the coating comprises at least 45% silica.
41. A coated substrate according to claim 40 wherein the coating comprises at least 50% silica.
42. A coated substrate according to any of claims 33-41 wherein the silica has a size of between 5 and 50 nanometers.
43. A coated substrate according to claim 42 wherein the silica has a size of between 10 and 40 nanometers.
44. A coated substrate according to claim 43 wherein the silica has a size of between 10 and 20 nanometers.
45. A coated substrate according to claim 44 wherein the silica has a size of about 16 nanometers.

46. A coated substrate according to any of claims 33-45 wherein the silica is not chemically bound to the rest of the coating.
- 5 47. A coated substrate according to any of claims 33-45 wherein the silica is chemically bound to the rest of the coating.
48. A coated substrate according to any of claims 33-46 wherein the coating further comprises an anchorage agent.
- 10 49. A coated substrate according to claim 48 wherein the anchorage agent comprises an amine material.
50. A coated substrate according to claim 49 wherein the amine material comprises a
- 15 diamine terminated substance.
51. A coated substrate according to claim 49 wherein the amine material comprises a monoamine terminated substance.
- 20 52. A coated substrate according to claim 49 wherein the amine material comprises a triamine terminated substance.
53. A coated substrate according to any of claims 50-52 wherein the substance is Poly(propylene oxide).
- 25 54. A printing method according to claim 50 wherein the substance is Poly-oxyethelene.
55. A coated substrate according to any of claims 33-54 wherein the substrate is acidic.
- 30 56. A coated substrate according to any of claims 33-54 wherein the substrate is coated with a polyamide coating between the coating containing silica and the sheet.
57. A coated substrate according to any of claims 33-56 wherein the sheet is PVC.

58. A coated substrate according to any of claims 33-56 wherein the sheet is PET.
59. A coated substrate according to any of claims 33-56 wherein the sheet is polycarbonate.
- 5 60. A coated substrate according to any of claims 33-59 wherein the coating is smooth.